'2

DPST--87-387

DE91 005116

TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

CC: D. L. McIntosh, 773-A
H. D. Harmon, 773-A
R. R. Fleming, 704-T
G. T. Wright, 703-H
G. M. Johnson, 703-H
D. F. Brown, 703-H
D. G. Piper, 676-8T
M. A. Hayes, 703-H
L. L. Kilpatrick, 773-A
S. B. Oblath, 773-A
J. L. Siler, 676-T
SRL Records (4)

July 28, 1987

M E M O R A N D U M

Received by OSTI

DEC 1 7 1990

TO: J. P. RYAN, 773-A

FROM: F. L. POY, 704-T

FOULING EFFECTS OF TRI-N-BUTYLPHOSPHATE ON REVERSE OSMOSIS PERFORMANCE AND TECHNIQUES FOR PERFORMANCE RECOVERY

INTRODUCTION

The F/H Effluent Treatment Facility (F/H ETF) must be on-line by November 1988 to treat the low level activity wastes presently being discharged to the F- and H- areas' seepage basins. The three main processes of the F/H ETF are filtration, reverse osmosis, and ion exchange. Any dissolved organics present in the F/H ETF's feed have the potential to affect operation of the reverse osmosis system. Earlier studies[1] with F/H ETF feed simulant and 70 volume percent kerosene and 30 volume percent tri-n-butylphosphate (TBP) additions showed that the kerosene/TBP mixture results in partial fouling of reverse osmosis membranes.

A more detailed analysis of the seepage basin feed has shown that TBP is the major dissolved organic compound.[2] Since it is dissolved (soluble to about 400 ppm at 25 °C), TBP will be present in the reverse osmosis feed unless removed by a means other than filtration. Thus the fouling effect of TBP (without kerosene) on reverse osmosis performance was investigated.

SUMMARY

Tri-n-butylphosphate (TBP) at expected feed levels was found to significantly degrade reverse osmosis performance. Therefore, it is recommended that TBP be removed from the stream before the reverse osmosis system. An alternative to an organic removal

system is the development of a reasor .e operating program allowing the reverse osmosis (RO) pe..ormance to drop to a certain point and then be recovered by some cleaning process. However, TBP removal is the preferred alternative because it avoids frequent RO cleaning, the associated waste volumes, and various potential operating problems. Futhermore, TPB removal may be necessary to meet the oil and grease discharge limit (10 ppm). TBP falls under the category of oil and grease, and preliminary tests indicate that all of the TBP entering the F/H ETF will enter the creek unless it is removed.

DISCUSSION

Tests were completed with TBP and F/H ETF simulant[3] on a single standard Filmtec SW30 reverse osmosis membrane. The membranes to be used in the F/H ETF are Filmtec SW30HR (high rejection) membranes. According to Filmtec, the standard and the high rejection membranes should behave similarly with respect to fouling. This report describes the results of the tests completed to determine the TBP fouling effects on reverse osmosis performance and the results of the various techniques used to recover the lost performance.

A 50 ppm TBP concentration is a reasonable average expected for the F/H ETF's feed stream. Reverse osmosis tests revealed that F/H ETF simulant feed containing 50 ppm (mg/L) TBP results in a ten percent loss in the RO's standardized permeate flow within five hours, and a 46% loss within 51 hours. Standardized permeate flow is a measure of RO performance. Filmtec suggests cleaning when this flow drops by ten percent. This corresponds to less than five hours of operation at 50 ppm TBP.

The RO tests demonstrated that RO fouling (lost performance) due to TBP is reversible. Organic cleaning with a caustic detergent solution restored 100% of the lost standardized permeate flow in all the cases. It was discovered for less severely TBP-fouled membranes, up to and including 29% lost standardized flow, that the circulation of filtered water through the RO membrane at low pressure and low flow also completely restores the lost flow. The water circulation method of cleaning TBP-fouled membranes is preferred over conventional chemical cleaning since no additional chemicals are necessary, resulting in a lower waste volume sent to saltstone.

It was discovered during the tests that the majority of TBP is rejected by the RO membrane. For feed streams containing up to 90 ppm TBP, the TBP concentration observed in the permeate stream was less than 5 ppm in all cases, and less than 1 ppm in most cases. It was also observed that higher feed TBP concentrations resulted in faster drops in RO performance. More data are required to quantify the relationship between TBP concentration and drop in RO performance.

Future tests include running feeds containing TBP through a single Filmtec High Rejection RO membrane to determine the mode of fouling. Plans also include running feeds through the F/H ETF's pilot system, the Experimental Contaminated Water Processing

Facility (ECWPF). The ECWPF contains a 40 gpm, 3 stage RO system of Filmtec high rejection membranes. The processing of effluent in this RO system closely resembles that of the F/H ETF's reverse osmosis system. Running feed containing TBP through the ECWPF would give a better measure of the extent of fouling expected in the F/H ETF's 3-staged system. Other tests will be directed at finding a feasible and reliable organic removal system.

EXPERIMENTAL

All of the RO tests described in this paper were conducted on a standard 2.5-inch diameter Filmtec SW30 reverse osmosis membrane. Various types of filters were used upstream of the membrane, including one and five micron polypropylene string-wound Filterite filters, and a CARRE ultrafilter.

Feed solutions for testing were prepared in 180 gallon tanks using process water, F/H ETF simulant chemicals[3] and when applicable, reagent grade tri-n-butylphosphate (TBP). When the Filterite filters were used, feed containing TBP was prepared by mixing the three ingredients in a 180 gallon tank. The feed would then be pumped through the Filterites and the RO membrane (See Figure 1a). When the ultrafilter was used, process water and simulant chemicals were mixed in a 180 gallon tank and filtered through the ultrafilter to another 180 gallon tank. The TBP would then be mixed in before being pumped through the RO membrane (See Figure 1b). The TBP was added post-ultrafiltration to avoid any rejection of TBP by the ultrafilter since the F/H ETF's filtration system will not reject dissolved TBP (i.e., all dissolved TBP will pass through the filter with the filtrate). Feed solutions for testing without TBP were prepared in the manners above, omitting the addition of TBP.

A table listing the various RO tests is shown in Table 1. All tests fall under one of two operating modes: constant feed pressure varying actual permeate flow or constant actual permeate flow varying feed pressure. Although both techniques were tested, the F/H ETF will operate under the latter conditions, maintaining a constant permeate flow of 20-30 GFD. The operating mode of constant feed pressure was used in tests to facilitate the operation of the system. Full-time monitoring is necessary on the test unit to maintain a constant actual permeate flow, but it is not necessary to maintain a constant feed pressure.

Graphs containing the normalized data may be found in Figure 3a through Figure 8. Plotted on these graphs are Standardized Permeate Flow (SPF) versus Time of Operation. The SPF is a measure of RO performance with a decreasing SPF indicating decreasing performance. The equation for the calculation of SPF is shown in Figure 2. In later tests, sodium chloride (2000 ppm) tests were also run through the RO membrane to give a reference point and intermittent data points of RO performance for a known solution. The same equation (with constants for NaCl) shown in Figure 2 was used to calculate SPF's for the sodium chloride tests. The RO membrane's salt (NaCl) rejection performance during these tests was monitored by measuring the feed and permeate conductivities.

More details concerning the tests listed in Table 1 are described in the remainder of this section. Discussion of the results may be found in the following section, Results and Observations.

I. Constant Feed Pressure Tests - Experimental

IA. Different Filter Cutoff Sizes - Experimental

Two tests were conducted to determine the effect, if any, that a filter cutoff size would have on the extent of fouling caused by TBP. Five and one micron Filterite filters were used in the two tests. Baseline simulant runs without TBP were conducted and then enough TBP was added to make 120 ppm TBP feed solutions. The system was run at a constant feed pressure of 620 psi and at total recycle where the RO permeate and concentrate streams are returned to the feed tank. The actual permeate fluxes for these tests began at 44 GFD and dropped with time as the membrane fouled. The resulting graphs for the 1 micron and 5 micron Filterite and RO runs are shown in Figures 3a and 3b, respectively.

IB. RO Performance Reaches Steady State Under Total Recycle Operation -Experimental

Two tests were conducted to study the steady state achieved by the RO when operated at total recycle with a feed containing TBP. Feed was prepared in both cases using an ultrafilter. Enough TBP was added in each test to make a 40 ppm TBP solution. One test was run with a single tank under total recycle with a constant feed pressure of 620 psi. The RO membrane was run until the RO performance (SPF) no longer dropped, a steady state was achieved. For the second test, two tanks of feed were prepared. One tank was run through the RO at total recycle and 620 psi feed pressure until a steady state was achieved (after about 22 hours). At this time, the second tank was run through the RO, also at total recycle and at 620 psi feed pressure until a second steady state was achieved. The starting actual permeate flux for both tests was 44 GFD and dropped with time as the membrane fouled. The resulting graphs for the single tank and the two tank steady state runs are shown in Figure 4.

IC. Acidified and pH-Adjusted Feed - Experimental

A test was conducted to determine whether the extent of TBP fouling would be less if the feed started out at an acidic pH and was then neutralized. This is the process which the actual F/H ETF feed will undergo. It was suggested that if TBP was present during the formation of solids, i.e., during the neutralization step, then perhaps the TBP would complex with the metal solids and be filtered out before reaching the RO membrane. To test this hypothesis, feed was prepared in the following manner: Process water was acidified to a pH of 2 using concentrated nitric acid. Enough TBP was added to make a 50 ppm TBP solution. (This last step was omitted for the simulant without TBP run.) Simulant chemicals were then added and finally the acidic solution was neutralized using 50 weight percent sodium hydroxide. This test was completed at a constant feed pressure of 300 psi and at total recycle. The filter used was a one micron Filterite. The actual permeate flux started at 21 GFD and dropped as the membrane fouled. The resulting graphs for the acidified and pH adjusted feed runs without and with TBP are shown in Figures 5a and 5b, respectively.

II. Constant Actual Permeate Flow Tests - Experimental

IIA. High Water Recovery Run followed by Low Circulation Cleaning - Experimental

A test was conducted to simulate the high water recovery to be obtained by the F/H ETF's RO system. This was achieved by using a single RO membrane and by recycling only the concentrate stream back to the feed tank. The constant permeate stream (21GFD) was diverted to the drain. The starting feed was 180 gallons of a 50 ppm TBP simulant solution. A one micron Filterite filter was used and the continuously concentrated feed passed through the filter before each pass through the RO (See Figure 1a). In this respect, the F/H ETF's RO system was not simulated since its filter is only present before the first pass.

After seven hours of feed concentrating, the water recovery was 71% (i.e., 71% of the original feed was removed as permeate). The F/H ETF will operate at an average water recovery of 90%. After 71% water recovery was obtained, the concentrated feed in the system was circulated for 16 hours (overnight) through the filter and RO at 30 psi and at a concentrate flow of 1 gpm. At this low pressure, the permeate flow is almost nonexistent and most of the solution circulates around the feed/concentrate side of the RO membrane. After the low circulation, a new batch of 50 ppm TBP feed was run through the system at total recycle and 21 GFD. An improvement in SPF was observed during this run. Process water (TBP-free) was then pumped through the filter and the RO membrane for another 16 hours at 30 psi and 1 gpm concentrate flow. Sodium chloride tests were run intermittently throughout this test. The resulting graph for the high water recovery run followed by low circulation cleaning is shown in Figure 6.

IIB. Single Pass, Total Recycle Run followed by Low Circulation Water Cleaning - Experimental

A test was conducted to simulate the first RO membrane of the F/H ETF's RO system. Feed containing 50 ppm TBP was prepared continuously and run at a single pass (no recycle) through a 1 micron Filterite filter followed by the RO membrane. Both the permeate (21GFD) and the concentrate streams were taken to the drain. This was continued for 9.5 hours after which a 180 gallon batch of 50 ppm TBP feed was run for 14 hours (overnight) through the system at total recycle. Standard sodium chloride tests were run intermittently to check the RO performance. After the feed recycle run, process water was circulated through the system at 30 psi and 1gpm concentrate flow over a 3 day weekend. The circulated water (less than 100 gallons) was kept at total recycle. A sodium chloride test was run after the 3 days of water circulation. The resulting graph from this single pass, total recycle run followed by a low circulation water cleaning is shown in Figure 7.

IIC. Single Pass Run - 51 hours followed by Multiple Step Cleaning - Experimental

Two tests were conducted to simulate extensive operation of the first membrane in the F/H ETF's RO system. One test used a 50 ppm TBP feed, the other test contained no TBP. In both tests, the feed was only passed through the system a single time (no recycle). Filterite filters were used and the actual permeate flow was held constant at 22 GFD. Each test lasted 51 hours. Following the test containing 50 ppm TBP, 30 gallons of a 2000 ppm sodium chloride solution was circulated through the system at 30 psi and 1 gpm concentrate flow. This was continued at total recycle for 53 hours. The feed pressure was periodically boosted to monitor the membrane's performance.

Following the sodium chloride circulation, process water was circulated through the filter and the RO membrane in the same manner for 16.5 hours. Then a sodium chloride test was run, followed by acid cleaning of the membrane. Ten gallons of a 0.25 weight percent oxalic acid solution was circulated through the membrane for 50 minutes at 30 psi and 1 gpm concentrate flow. The membrane was then allowed to soak for 30 minutes. Acid cleanings are recommended for inorganic fouling. A sodium chloride test was run after the acid-cleaned RO membrane was flushed with water. The lost SPF was still not completely restored after acid cleaning. Thus the acid cleaning was followed by a caustic detergent cleaning. Such cleaning solutions are recommended for organic fouling. Ten gallons of a 0.5 weight percent sodium lauryl sulfate and 0.05 M sodium hydroxide solution was circulated through the membrane for 30 minutes at 30 psi and 1 gpm concentrate flow. The membrane was then allowed to soak for 1.5 hours. After the membrane was flushed with water, a sodium chloride test was run. The graph containing the results of this single pass run followed by multiple step cleaning is shown in Figure 8.

RESULTS AND OBSERVATIONS

Tri-n-butylphosphate lowers the performance of Filmtec thin-film composite RO membranes below the desired levels of operation. The results of the tests are shown in Figures 3a to 8 and will be referred to in the course of the discussions in this section. The figures contain graphs of the Standardized Permeate Flow (SPF) versus Time of Operation. A drop in SPF corresponds to decreasing RO performance. Filmtec suggests cleaning when the SPF drops by ten percent. The F/H ETF will operate until a maximum drop of 20% in SPF, at which time the RO will be cleaned. The remainder of this section will be devoted to the discussion of results obtained from the individual tests described in the Experimental Section.

I. Constant Feed Pressure Tests - Results and Discussions

IA. Different Filter Cutoff Sizes - Results

Earlier studies[1] indicated that TBP may cause RO fouling. A set of tests has determined that the cutoff sizes of filters used in our tests does not affect RO fouling. If the results revealed that the filter size did affect RO fouling then the pre-filter would have been carefully chosen to duplicate the F/H ETF's expected filtrate quality. Filterite filters of one and five micron (nominal) cutoff sizes were tested with a simulant feed containing 120 ppm TBP (See Figures 3a and 3b). Most of the fouling, as observed in the decreasing SPF, occurred during the first hour. In both cases, the SPF had dropped by 35% of its initial value and levelled out. Therefore, for the different filter cutoff sizes dealt with in these tests, there is no noticeable effect on fouling due to the filtration cutoff size.

IB. <u>RO Performance Steady State Under Total Recycle Operation - Results</u>

When a system operates under total recycle in the presence of TBP, the SPF drops to a steady state level after a period of time but will drop to another steady state level if another feed batch is put on-line at total recycle. A set of tests was designed after many tests were run at total recycle. In all of these recycle tests, the SPF dropped to a point and remained level for the duration of the run.

It was hypothesized that the recycled feed and the RO membrane reach a steady state such that no more fouling occurs. Two tests were conducted to test this hypothesis, one with a single tank of feed at total recycle and the second with two tanks of feed run consecutively at total recycle. Feed for both tests contained 40 ppm TBP. Figure 4 shows a steady state SPF being reached with each feed tank being recycled. The test conducted with only a single tank reaches a steady state SPF after approximately 22 hours of operation. The SPF had dropped by 13 % after 22 hours and by a total of 16% after 51 hours. The test conducted with two tanks reaches two different steady states; one after each tank was recycled. The first tank was run for 22 hours by which time the SPF had dropped 13% of its initial value, as was the case for the single tank only.

When the second tank was put on-line and run for 29 additional hours (or a total of 51 hours), the SPF had reached a second steady state. The SPF at this time had dropped by a total of 30% since the beginning of the test. This 30% drop in SPF is 14% greater than that obtained in the test with only a single tank (16%) within the same period of 51 hours. Figure 4 also shows that the majority of the drop in SPF occurs soon after the start of each tank. The results of these tests brings up the question as to what would happen with a test completed without recycle, i.e., with continuous fresh feed at a single pass. TBP was still present in the feed once the systems reached a steady state. A plausible explanation for what was observed is that the TBP is complexing with some compound, perhaps a metal compound, which is causing fouling of the RO membrane. Once the supply of this compound has been exhausted, the membrane does not foul any further.

Rate of Fouling versus TBP Concentration - Results

The rate of fouling (drop in SPF) is higher for higher feed concentrations of TBP. The feeds for the test results shown in Figures 3a and 3b contained 120 ppm TBP. The feed for the test results shown in Figure 4 contained 40 ppm TBP. In all these tests, the system was operated at a constant feed pressure of 620 psi. The tests containing 120 ppm TBP show a drop in SPF of over 30% after 22 hours whereas the test with only a single tank of 40 ppm TBP, the SPF drops by only 13% after 22 hours. The rate of fouling was observed to be higher for the higher TBP concentrations (for 120 ppm over 40 ppm). A more encompasssing quantitative statement relating the rate of fouling to the TBP concentration would require further tests.

IC. Acidified and pH Adjusted Feed - Results

Manipulation of pH during feed simulant preparation does not affect the rate of fouling caused by TBP. As a result of previous tests, it was hypothesized that the TBP may be complexing with one of the metal compounds in the simulant and causing the RO fouling. Then once this compound is spent, the membrane will not foul any further. This would explain the steady state reached after hours of operation at total recycle. This brought up questions concerning the method of simulant preparation. Simulant is typically prepared by combining process water, simulant chemicals and TBP (for use with Filterite filters). However, the TBP that would enter the F/H ETF originates from the evaporator overheads, which is often acidic. The feed would then be neutralized just before feeding the F/H ETF. Assuming that the TBP is complexing with a metal compound, perhaps if the TBP had a longer contact time with such compounds and was present during their formation then it is possible that the TBP may be removed with the solids in filtration before RO. This led to testing a new method of simulant preparation. TBP (enough for a 50 ppm solution) was combined with the simulant chemicals in acidified process water and then neutralized. This solution was then run through one micron Filterite filters and through the RO membrane at total recycle. As shown in Figure 5, the SPF dropped 15% after 21 hours. This is comparable to the 13% loss in SPF observed after 22 hours in an earlier test (See Figure 4) whose 40 ppm TBP feed had not been pH manipulated. And as in other recycle runs, Figure 5 shows that the majority of the SPF is lost during the beginning of the run. Apparently, the acidification and pH adjustment does not affect the rate of fouling due to TBP. This does not however rule out the possibility that the TBP is complexing with something small enough to pass through the filters and reach the RO membrane.

II. Constant Actual Permeate Flow Tests - Results and Discussions

IIA. High Water Recovery Run followed by Low Circulation Cleaning - Results

The SPF monotonically dropped 26% within seven hours as the water recovery rose to 71%. The lost SPF was restored by low pressure, low circulation of water through the membrane. The F/H ETF's RO system will operate at approximately 90% water recovery [i.e., 90% of the feed stream will be permeate (clean product) which will go on to ion exchange]. As the feed was concentrated around the single RO membrane, the SPF dropped and the TBP concentration increased (See Figure 6a). By the time 71% water recovery was achieved, the feed was analyzed for total organic carbon (TOC) and the calculated amount of TBP present was 90 ppm. The SPF had dropped by 26%. After this run, the resulting concentrated feed was circulated through the RO membrane for 16 hours (overnight) at low pressure and low flow. An improvement was observed in the SPF when another batch of 50 ppm TBP feed was run through the membrane (See Figure 6b). This rise in SPF with low circulation of concentrated feed prompted a low circulation of water (TBP-free) for 16 hours through the membrane. After the water circulation, a sodium chloride test indicated that 100% of the lost performance (SPF) was recovered (See Figure 6c).

The TBP concentrations shown on Figures 6a through 6c are numbers calculated from TOC analyses and are suspect. The starting concentration, according to analysis, was calculated to be 32 ppm while the theoretical concentration was 50 ppm. The actual concentration is probably much closer to the theoretical amount. The numbers stated elsewhere in this report are theoretical values. Tests indicate that TBP concentrations calculated from the standard TOC results from the analysis technique used in SRL are lower than the actual TBP concentrations. The actual TBP concentrations were checked via TBP extraction followed by gas chromatography for compound identification. For actual TBP concentrations of 30 to 50 ppm, the TOC analyses indicate only 85-90% of the actual values. The accuracy of TOC analysis for TBP identification drops with increasing TBP concentration. For actual TBP concentrations in the 200's (ppm) range, the TOC analyses indicate only 60% of the actual values. It has also been observed that for the same feed sample, the longer the shelf life prior to TOC analysis, the lower the TOC results.

Rejection of TBP by Reverse Osmosis - Results

The majority of the TBP fed to the reverse osmosis membranes is rejected. For TBP concentrations up to and including 90 ppm (calculated from TOC analyses), the calculated TBP concentration in the permeate was less than 5 ppm for all cases. The rejection of TBP is demonstrated in the high water recovery run (See Figure 6a). The feed concentration of TBP is constantly rising as the permeate is drawn off and the concentrate is being recycled back to the feed. (It should be kept in mind that the TBP concentrations shown in Figure 6a are suspiciously low.)

IIB. Single Pass, Total Recycle Run followed by Low Circulation Water Cleaning - Results

An RO test membrane operated under F/H ETF operating conditions showed a 22% drop in SPF after 9.5 hours of operation (See Figure 7) with a 50 ppm TBP feed. One hundred percent of the lost SPF was restored within 72 hours (3 day weekend) of low pressure and low flow water circulation through the membrane. The RO membrane was continuously fed in the single pass (no recycle) mode for 9.5 hours and was operated at a constant 22 GFD permeate flux. After 9.5 hours, 180 gallons of the same feed makeup was run at total recycle for 16 hours (overnight). The SPF also dropped during the recycled feed run. After ten hours of recycle, the SPF dropped an additional 6% (total of 28%) and levelled out. The fact that the SPF continues to drop supports the possibility that the TBP may be complexing with some compound that is adsorbing onto the membrane. The fouling components appear to remain on the membrane as long as the flows and pressures are in their normal operation values. This implies that as long as there is a source of foulant, the SPF will continue to drop. Of course, there must be some limit to the extent of fouling; however, this limit is unknown.

IIC. Single Pass Run - 51 hours followed by Multiple Step Cleaning - Results

An RO membrane operated under F/H ETF operating conditions with a 50 ppm TBP feed solution showed a 47% drop in SPF after 51 hours of operation (See Figure 8a). No change in SPF was observed in a similar run completed without TBP (Also in Figure 8). For the test containing TBP, low pressure, low flow circulation of TBP-free solutions did not restore all of the lost SPF. Ultimately, chemical (detergent) cleaning for organic fouling was necessary to recover 100% of the lost SPF. In this test, the RO membrane was continuously fed in the single pass (no recycle) mode for 51 hours with a 22 GFD permeate flux. After 9.5 hours of operation in the single pass mode, the SPF had dropped by 14% compared to a 22% drop after 9.5 hours in the Single Pass, Recycle Run discussed earlier. After 51 hours, the SPF had dropped a total of 47%. The 47% drop in SPF corresponded to a required 69% increase in original feed pressure to maintain the constant actual permeate flux.

Many types of cleaning were tried before 100% of the SPF was restored (See Figure 8). About 70 hours of low pressure, low flow circulation of water and a 2000 ppm sodium chloride solution through the membrane only restored 87% of the lost SPF. A subsequent oxalic acid cleaning, for inorganic fouling, restored an additional 7% (total of 94% recovered). Ultimately, a sodium lauryl sulfate and sodium hydroxide solution, for organic fouling, restored the remainder of the lost SPF.

Low pressure, low circulation with water and salt water did not restore the flux within 70 hours, a period beyond which would be reasonable for the F/H ETF operation. In the single pass run shown in Figure 7, the SPF had dropped by only 28% and this was completely restored by low pressure, low flow water circulation at some point within 72 hours. There appears to be a point of RO fouling beyond which water circulation is no longer a reasonable alternative to chemical cleaning.

A 69% increase in feed pressure, as observed in the test membrane, would not be acceptable for F/H ETF RO operation over a long period of time. The ETF will use Filmtec high rejection SW30HR membranes in a three stage RO system. For the average expected salt concentration (equivalent to the simulant concentration), the first stage feed pressure will be 500 psi and the third stage pressure will be boosted to 650-700 psi. The maximum operating pressure at which the RO membranes may be operated is 1000 psi. The majority of the available feed pressure margin when operating with an average salt concentration cannot be taken up by fouling. If the feed's salt concentration increases, additional feed pressure must be applied to overcome the higher osmotic pressure inherent of the solution's higher salt concentration and to maintain a constant permeate flux.

Filmtec suggests cleaning when there is a ten percent loss in flux. This corresponds to an operating time of less then five hours for a 50 ppm TBP feed solution (Figures7 and 8). It is recommended that the TBP be removed before the F/H ETF's RO system. If TBP is not removed, the RO system will require frequent cleaning, and because the majority of the TBP remains in the RO concentrate, the TBP will make its way to the creek via the evaporator overheads[4]. Preliminary tests show that all of the TBP entering the evaporator will be carried overhead, flow through a resin column, and be discharged into the creek. The discharge of TBP to the creek presents another problem. TBP is freon extractable and falls under the category of oil and grease. The F/H ETF has an oil and grease discharge limit of 10 ppm. Fifty parts per million TBP is a reasonable estimate for the average TBP concentration expected in the feed. Thus, most of the TBP will have to be removed at some point to meet the oil and discharge criteria. By removing before the RO, we protect the RO membranes as well as meeting the oil and grease discharge limits. This also protects the system from the scenario of the RO passing permeate containing greater than 10 ppm TBP.

CONCLUSIONS

It is recommended that an organic removal system be installed before the F/H ETF's reverse osmosis system. Tests show that TBP at expected feed levels lowers the RO performance below desired levels of operation within a short period of time. A fifty-one hour single pass (no recycle) run demonstrated this using a 50 ppm TBP solution operating at 22 GFD actual permeate flux, within the F/H ETF's 20-30 GFD range. Filmtec suggests cleaning the RO membranes after a ten percent loss in flux is observed. The fifty-one hour run showed a 10% drop in standardized permeate flow (SPF) within 5 hours, a 14% drop within 9.5 hours and a 46% drop within 51 hours. No signs of the SPF levelling out was observed even after 51 hours. A similar run completed without TBP showed no significant change in SPF (See Figure 8).

The F/H ETF's plans are not to let the RO system's SPF drop more than 10-20%. The 46% drop in SPF on the test membrane corresponded to a 69% increase in feed pressure necessary to maintain a constant actual permeate flux. The F/H ETF's RO system consists of three stages. For average salt concentrations, the first stage feed pressure will be 500 psi and the third stage feed pressure will be 650-700 psi. The highest allowable operating pressure for the membranes is 1000 psi. The majority of the feed pressure margin must be maintained for the times when the feed's salt concentrations are above average. During these times, the membranes must be operated at higher feed pressures to overcome the additional osmotic pressure exerted by the higher salt concentrations. Thus, the F/H ETF cannot allow their SPF to drop below 10-20% of its initial value for any long period of time.

The drops in RO performance (measured by drops in SPF) were determined to be reversible. In all tests, the lost SPF was completely restored by cleaning. Manufacturers recommend that organically-fouled membranes be cleaned by a basic soap solution. A 0.5 weight percent sodium lauryl sulfate and 0.05 M sodium hydroxide solution was successful in completely restoring lost fluxes, including a case with a 46% drop in SPF (See Table 1).

It was also demonstrated that lost SPF is partially and in some cases fully recovered by recirculation of water (TBP-free) at 30 psi and 1 gpm concentrate flow over a period of time. For less severely fouled membranes, including a case with a 28% loss in SPF, 100% of the SPF was recovered by this low circulation method. The membrane which had a 28% drop in SPF recovered 100% of its SPF within 72 hours. The actual time at which the SPF was completely restored is not known since the performance was not checked at any point within the 72 hours (3 day weekend) of circulation . Exact circulation times necessary for full SPF recovery have to-date not been determined. Water circulation for flux restoration purposes is preferable over chemical (detergent) cleaning because 1) No cleaning chemicals are necessary and 2) Less waste is sent to saltstone since a detergent cleaning solution and the initial flush water from the RO must bypass the evaporator and be fed with evaporator concentrate to saltstone. This is avoided with the use of water for cleaning.

Frequent RO cleaning to maintain a constant actual permeate flux is an alternative to organic removal for the F/H ETF. However, organics will have to be removed to meet the oil and grease discharge limit of 10 ppm for the facility. TBP is extractable by freon and thus, falls under the category of oil and grease. The average TBP concentration going to the seepage basins is presently 30 ppm. This average is low due to the recent higher than normal downtime of the canyons. When the canyons are operating, the average TBP concentration is over twice this level, or greater than 60 ppm. Preliminary tests indicate that any TBP fed to the evaporator will go to the overheads and ultimately to the stream if it is not removed[5]. For RO feeds containing up to 90 ppm TBP, all permeate streams contained less than 5 ppm TBP and most cases less than 1 ppm. The majority of remaining TBP fed to the RO winds up in the RO concentrate stream which feeds the evaporator. The TBP in both the RO permeate and concentrate streams would ultimately wind up in the creek. Therefore, unless it is removed somewhere in the system, whatever TBP acomes into the F/H ETF will be discharged to the creek.

In order to meet discharge limits, the TBP must be removed from the stream. This may be done in several ways including adsorption by carbon or nonfunctional resins, and destruction by ozonation. Since organic removal is inevitable for the F/H ETF, the organic removal system should be placed before the RO to avoid the need for frequent cleaning of the RO membranes. If the organic removal system is not placed before RO, cleanings may be more frequent than every five hours since the TBP concentrates as it travels through the RO system. Tests show that higher TBP concentrations may result in faster fouling and thus require more frequent cleanings. Tests completed at total recycle containing 40 ppm (See Figure 4) and 120 ppm TBP (See Figure 3) showed 13% and 30% drops in SPF, respectively after 22 hours of operation. To quantify this, more tests would be required. However, the F/H ETF's RO system will be concentrating the feed TBP concentration as it travels through the RO.

Presuming that Filmtec High Rejection Membranes (SW30HR) behave similarly to the SW30 membrane tested here, TBP has the potential to degrade, unacceptably, the performance of Reverse Osmosis in the F/H ETF. In practice, the fouling mechanism may be even more detrimental to the "tighter" higher rejection membranes. Therefore, to avoid frequent RO cleanings, which may prove impractical with the F/H ETF feed fluctuations, it is recommended that an organic removal system be installed before the F/H ETF's RO system. An organic removal system is also justified since it is necessary to meet the facility's oil and grease discharge limits.

REFERENCES

1. F. L. Poy, "Pilot-Scale Tests Results for the F/H ETF: Effect of Tributylphosphate/Kerosene on Reverse Osmosis Productivity", DPST-86-485TL, June 25, 1986.

2. S. B. Oblath, DPST in draft.

3. J. P. Ryan, "Separations Areas Effluent Treatment: The Preparation of a Simulated Effluent For System Development and Testing", DPST-84-287, February 8,1984.

4. S. B. Oblath, DPST in draft.

FLP

Table 1. Test Conditions for Reverse Osmosis Tests

I. Constant Feed Pressure, Variable Permeate Flow Tests

Figure Number	Theoretical TBP Concentration (ppm)	Type of Filter	Recycle or Single Pass	Feed Pressure (psi)	Time of Operation (hrs)	Cleaning Solution(s) Used¥
3a	120	1 micron Filterite*	Total Recycle	620	67	Organic
3b	120	5 micron Filterite*	Total Recycle	620	25	Organic
4	40	CARRE Ultrafilter†	Total Recycle	620	51	Organic
4	40	CARRE Ultrafilter†	Total Recycle^Δ	620	51	Organic
5a	0	1 micron Filterite*	Total Recycle°	300	23	Organic
5b	50	1 micron Filterite*	Total Recycle°	300	20	Organic

Table 1 is continued on the next page.

Table 1 (cont). Test Conditions for Reverse Osmosis Tests

II. Constant Actual Permeate Flow, Variable Feed Pressure Tests

Figure Number	Theoretical TBP Concentration (ppm)	Type Filter	Recycle or Single Pass	Permeate Flux (GFD)	Time of Operation (hrs)	Cleaning Solution(s) Used¥
6a-6c	50 (at beginning)	1 micron Filterite*	Concentrate Recycle◊	21	7	Water
7	50	1 micron Filterite*	Single Pass/ Total Recycle	22	9.5/14	Water
8	50	1 & 5 micron Filterite*	Single Pass	22	51	Water/ Inorganic/ Organic

* Polypropylene string-wound Filterite cartidge filters
† Sintered metal tubes with zirconium oxide membrane
Δ One tank run at total recycle followed by a second tank at total recycle
° Acidified and pH-adjusted feed
◊ Concentrate recycled to feed tank; permeate taken to drain

¥Cleaning solutions:
Organic - 0.5 weight percent sodium lauryl sulfate/ 0.05M sodium hydroxide
Water - Water circulation at 30 psi, 1 gpm concentrate flow
Inorganic - 0.25 weight percent oxalic acid

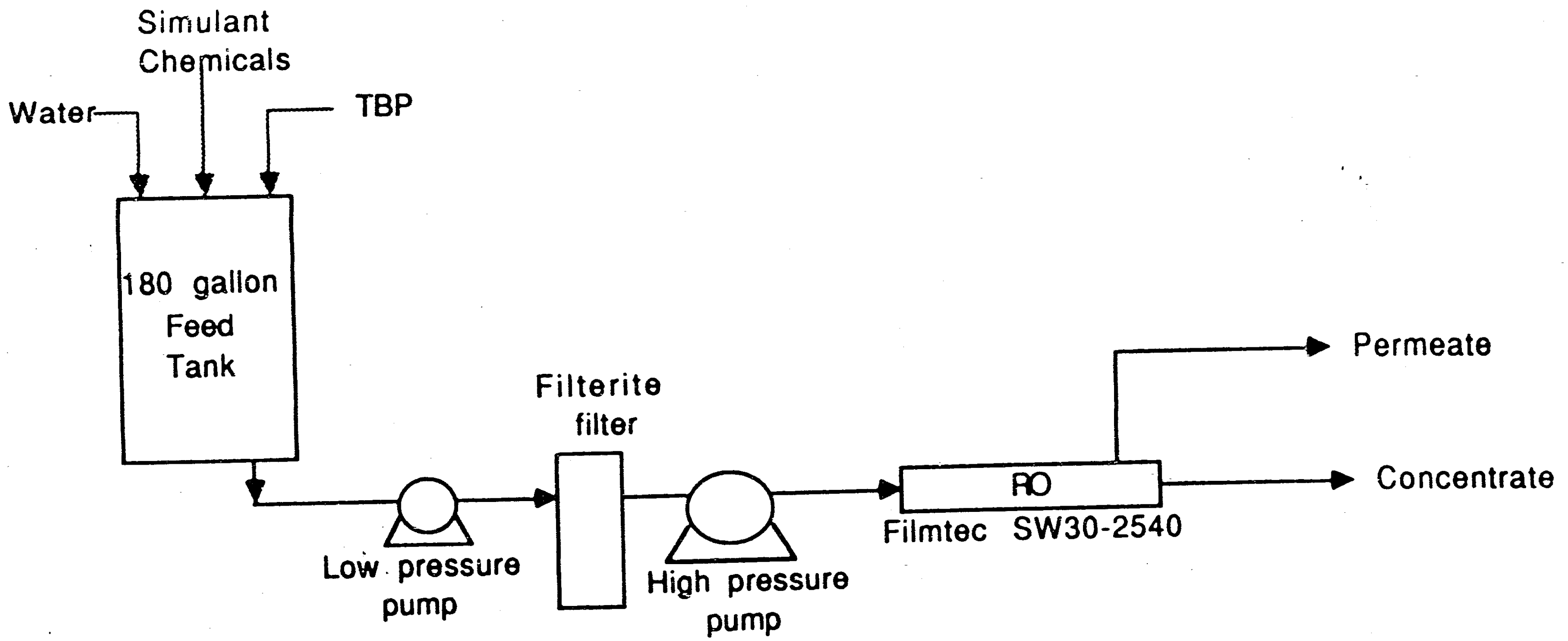


Figure 1a. Reverse osmosis system flow schematic for use with Filterite filters

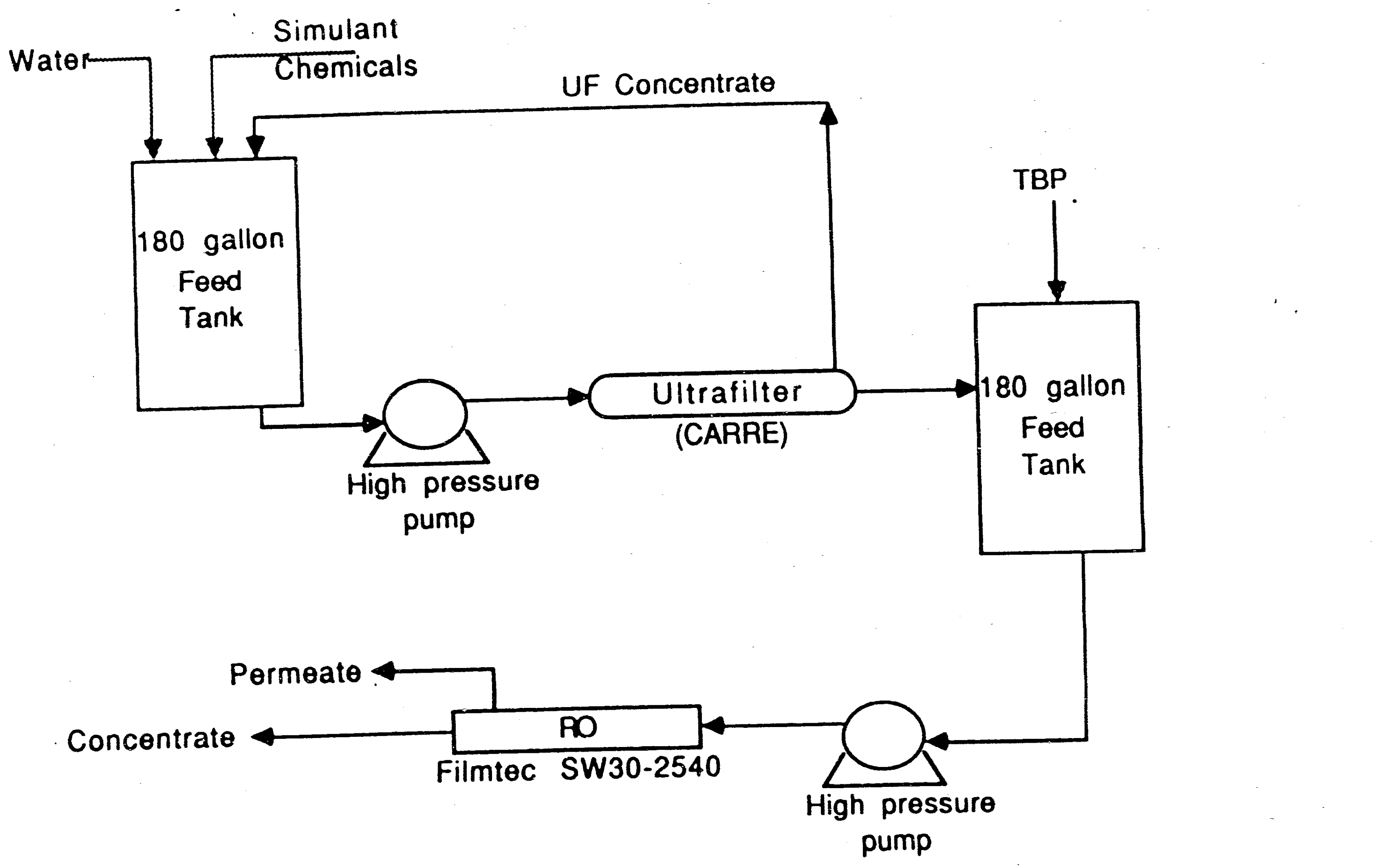


Figure 1b. Reverse osmosis flow schematic for use with CARRE ultrafilter

STANDARDIZED PERMEATE FLOW

$$\text{Standardized Permeate Flow (SPF)} = \frac{\text{Actual Permeate Flow}}{(TCF) \cdot (PCF)}$$

where TCF = Temperature Correction Factor = $1.03^{(T-25°C)}$
where T = system temperature, °C

$$PCF = \text{Pressure Correction Factor} = \frac{P_f-(\Delta P_{brine}/2)-P_{perm}-\Pi}{(800\text{-}20/2\text{-}0\text{-}375)\text{psi}\dagger}$$

where P_f = feed pressure, psi
ΔP_{brine} = brineside pressure drop, psi = $P_f - P_{concentrate}$
P_{perm} = permeate pressure, psi

$$\Pi = \text{osmotic pressure}^*, \text{psi} = k_{ave,brine} \frac{1000\text{ppm } NaNO_3 (7.72\text{psi})}{1190\mu\text{mho/cm } (1000\text{ppm } NaNO_3)}$$

where k = conductivity, µmho/cm
and $k_{ave,brine} = (k_{feed} + k_{concentrate})/2$

† (800-20/2-0-375)psi = Reference point (seawater solution). Numbers correspond to the same variables in the numerator.

* The conversion factors are for $NaNO_3$ and is good for the F/H ETF simulant which is >80% $NaNO_3$ by concentration.

Figure 2. Equation for Calculating Standardized Permeate Flow

Figure 3a. RO Standardized Permeate Flow vs. Time of Operation

System: 120 ppm TBP, 1µ Filterite, Total Recycle

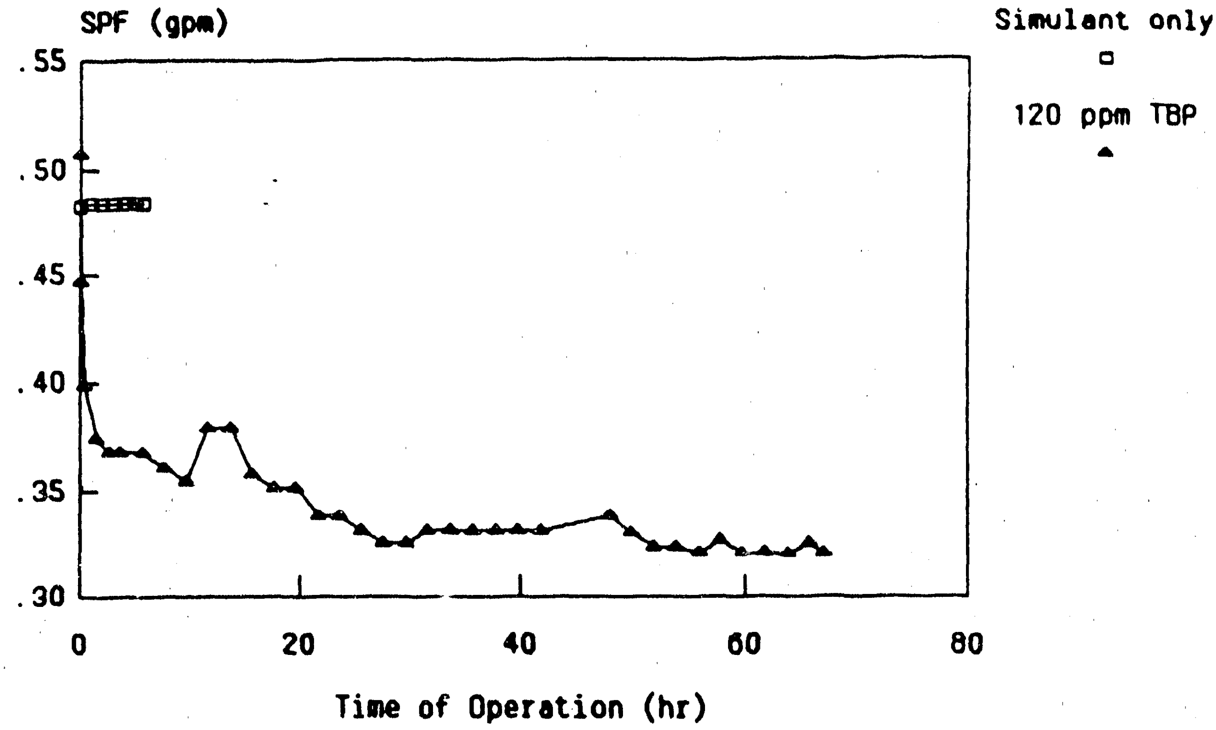


Figure 3b. RO Standardized Permeate Flow vs Time of Operation

System: 120 ppm TBP, 5 µ Filterite, Total Recycle

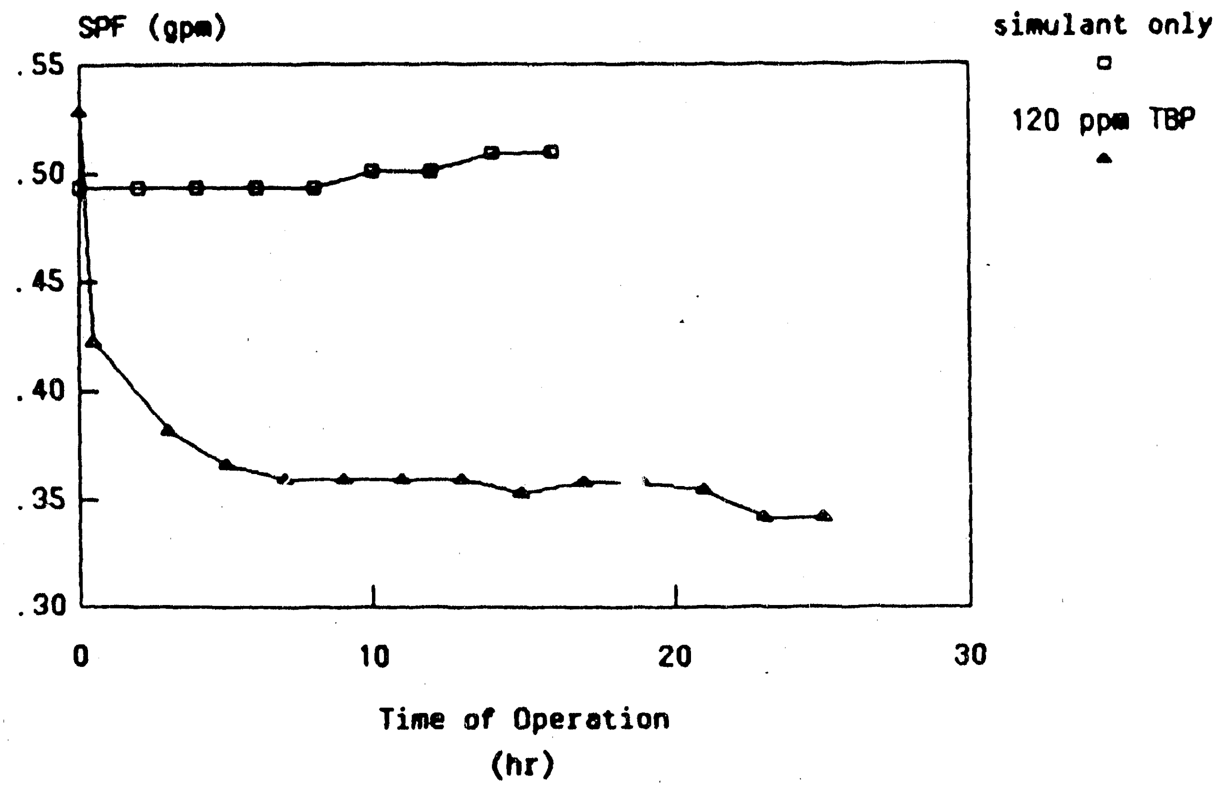


Figure 4. RO Standardized Permeate Flow vs Time of Operation

System: 40 ppm TBP per tank, Each tank at Total Recycle

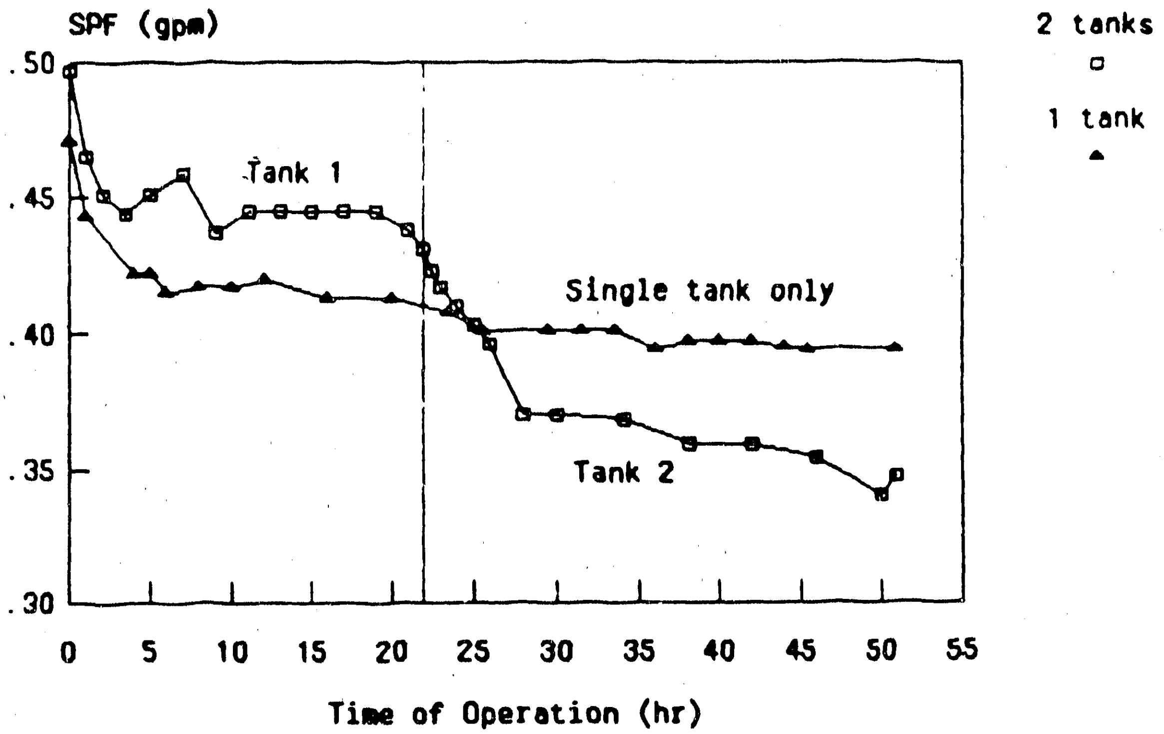


Figure 5a. RO Standardized Permeate Flow vs Time of Operation

System: Acidified, pH Adjusted F/H ETF Simulant, No TBP

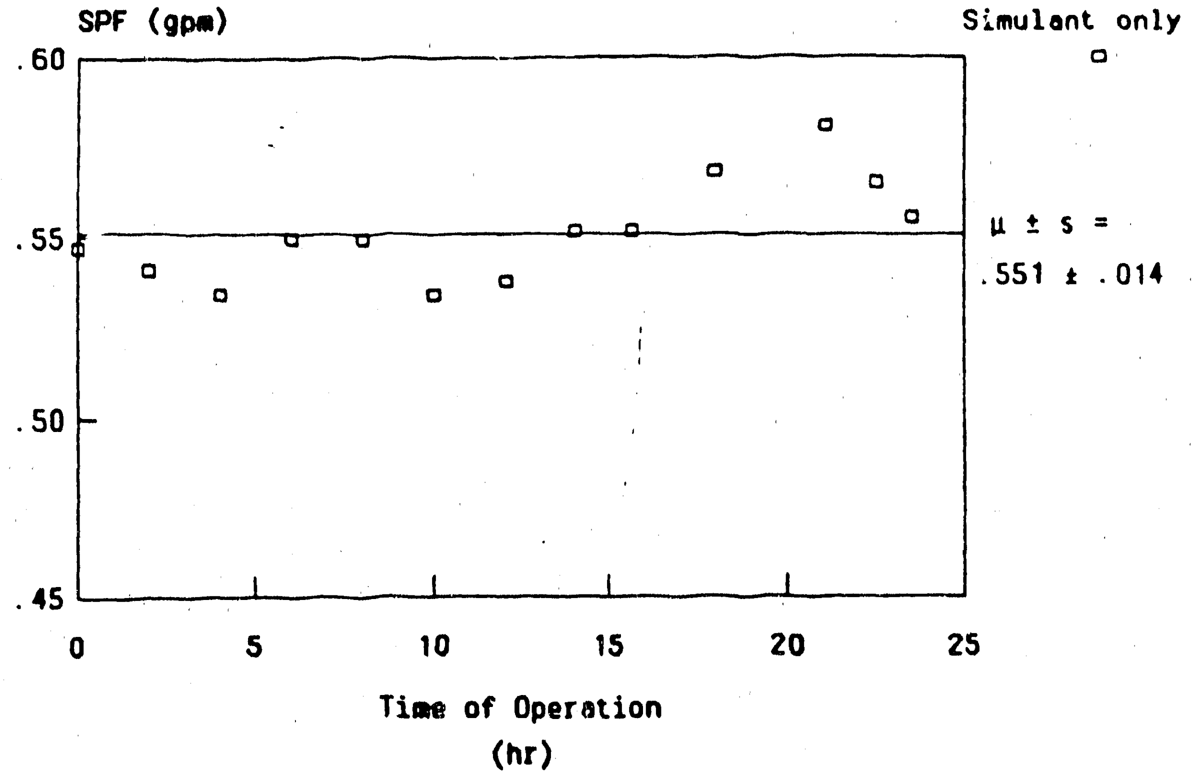


Figure 5b. RO Standardized Permeate Flow vs Time of Operation

System: 50 ppm TBP, Acidified/pH Adjusted Feed, Total Recycle

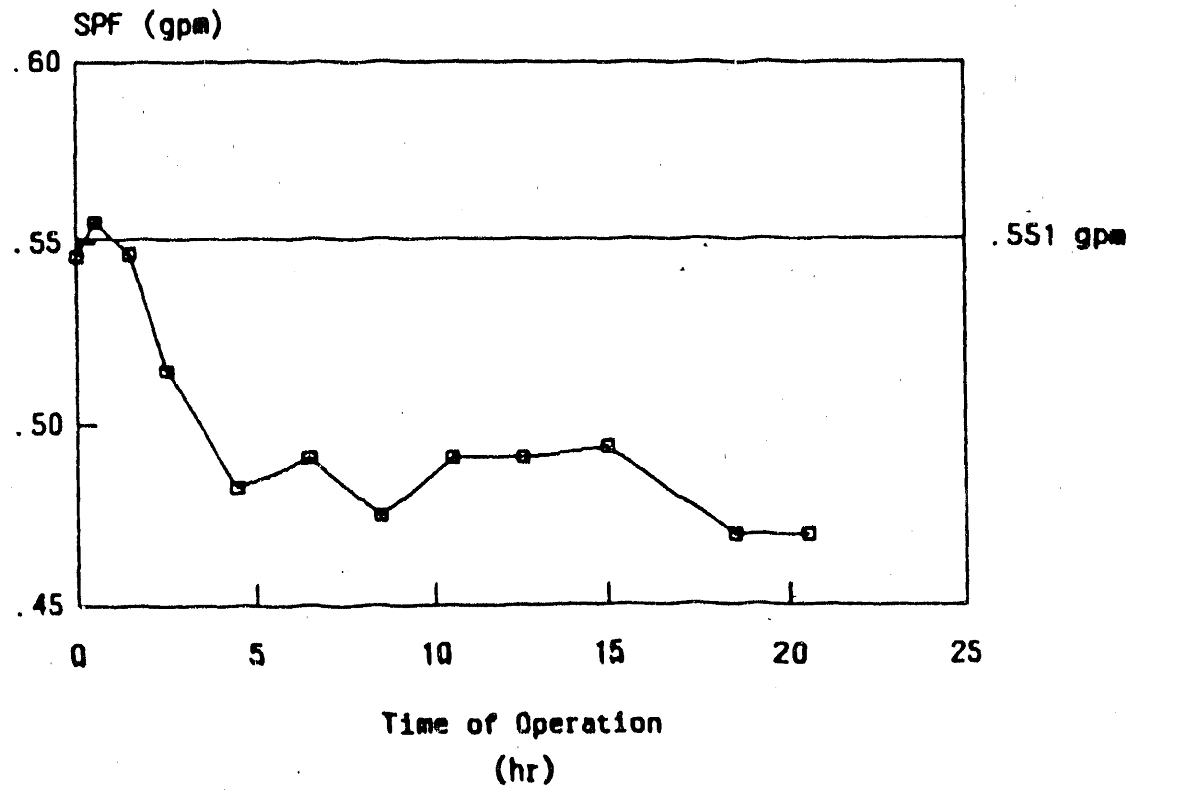


Figure 6a. RO Standardized Permeate Flow vs Time of Operation

System: High Water Recovery Run (Recycled Concentrate)

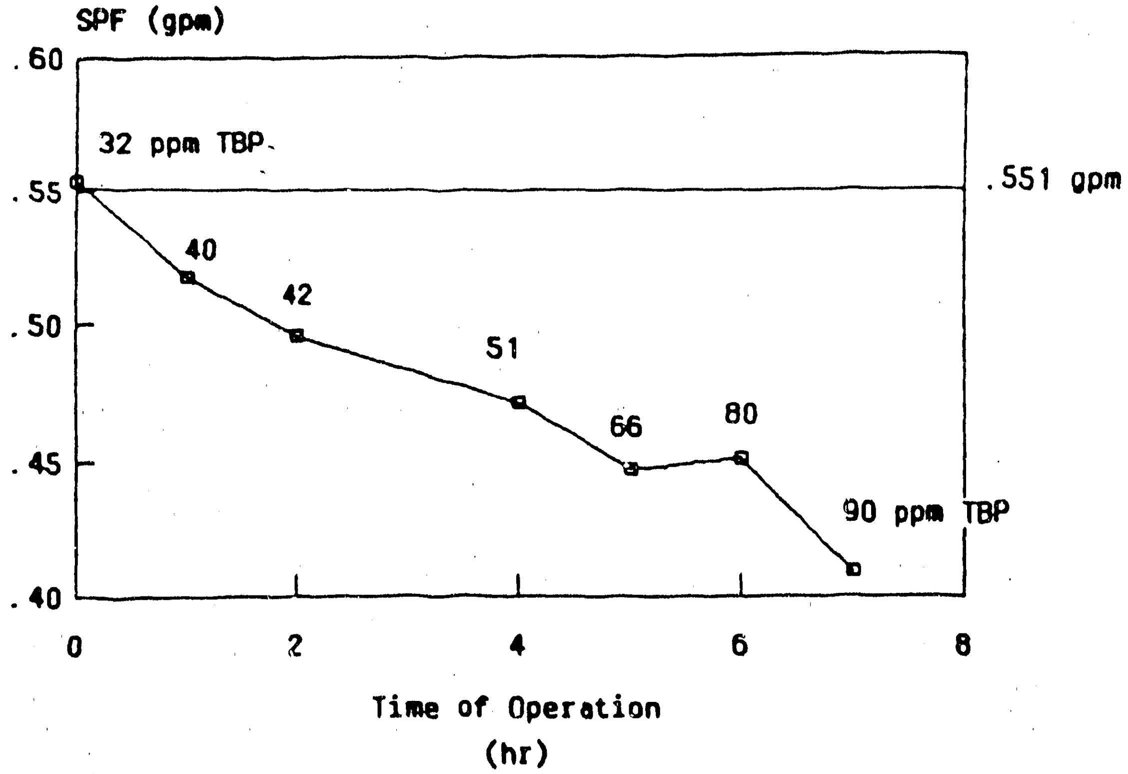


Figure 6b. RO Standardized Permeate Flow vs Time of Operation

System: Figure 6a with low circulation of concentrated feed and Recycled 32ppm feed

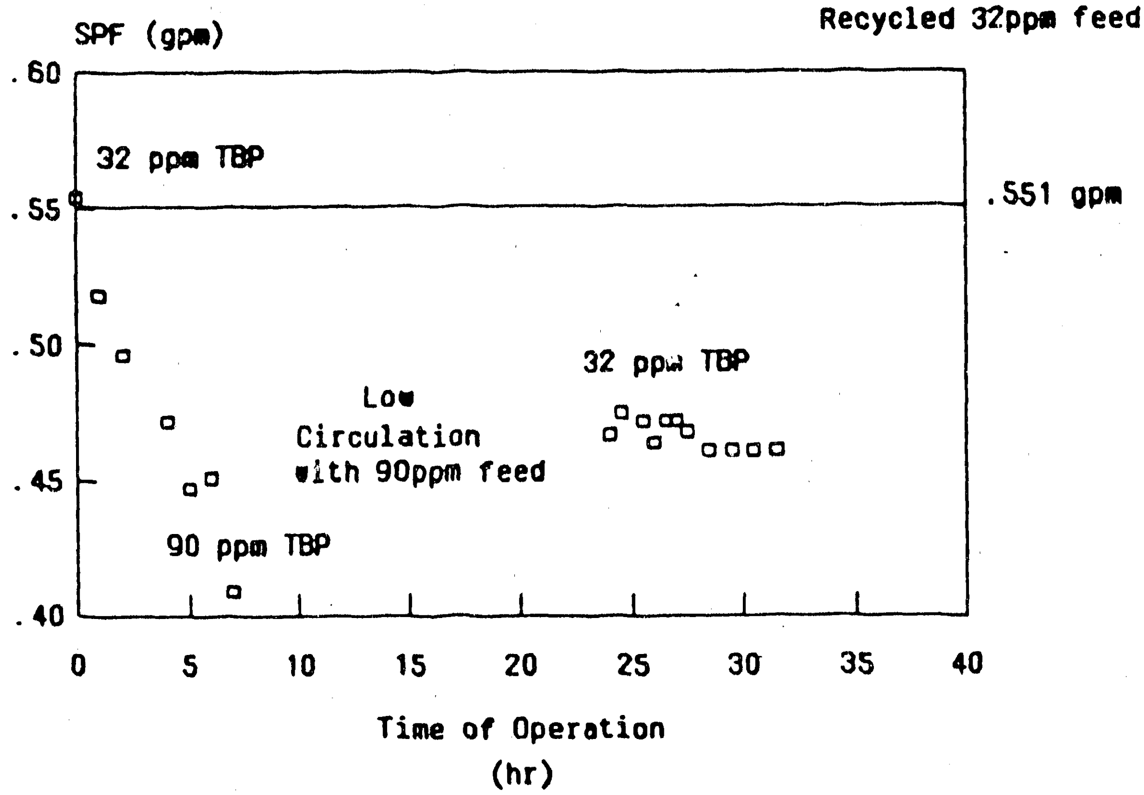


Figure 6c. RO Standardized Permeate Flow vs Time of Operation

System: Figure 6b with low circulation of water

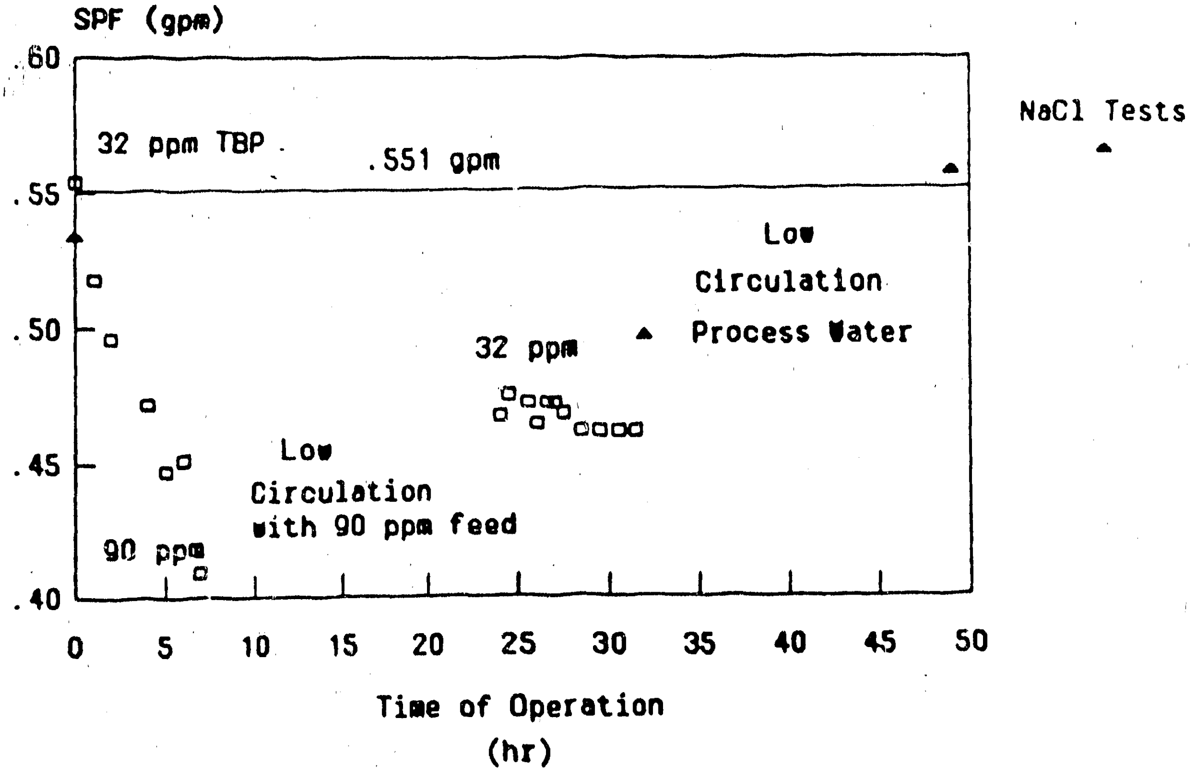


Figure 7. RO Standardized Permeate Flow vs Time of Operation

System: Single Pass(9.5 hrs), Recycled feed, low circulation cleaning

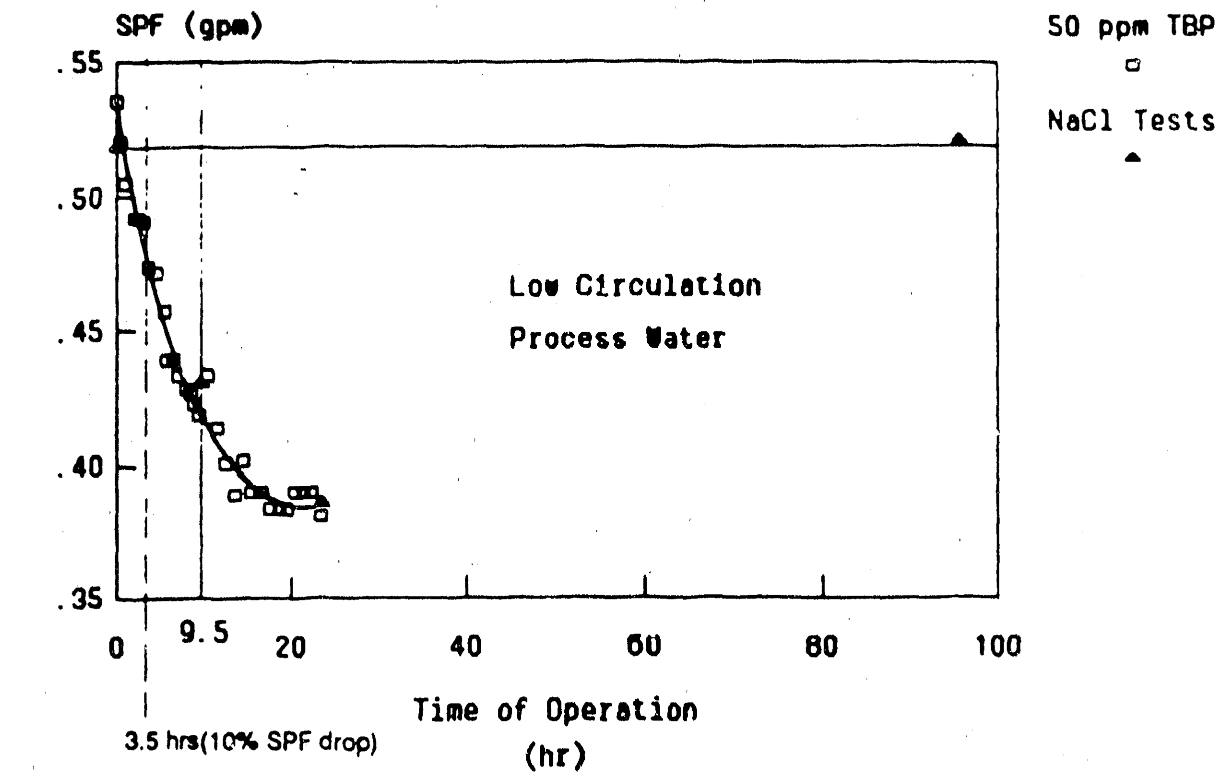
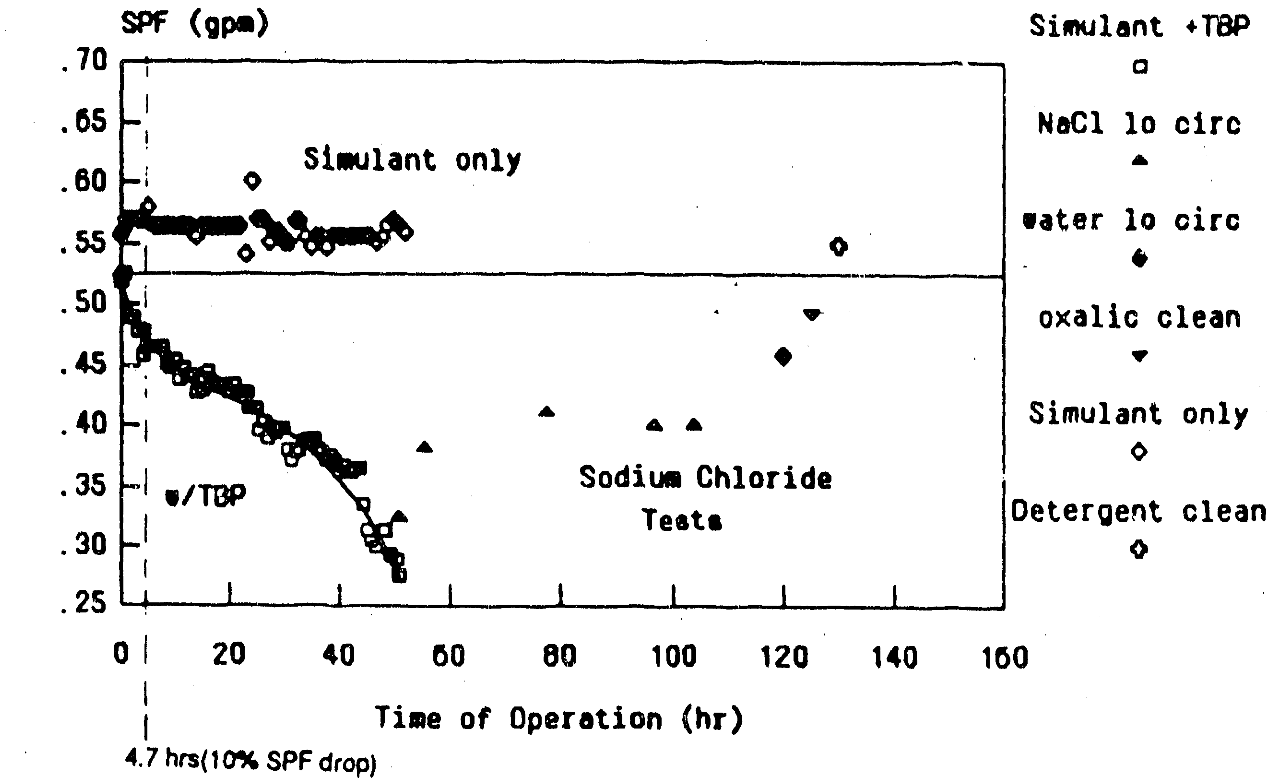


Figure 8. RO Standardized Permeate Flow vs Time of Operation

System: 50 ppm TBP, Single Pass with multiple step cleaning



END

DATE FILMED

02 / 13 / 91